A. Using a Coffee-Cup Calorimeter

Polystyrene coffee cups make excellent calorimeters because of their ability to block the passage of heat. The complete calorimeter consists of two nested 6-ounce cups, a top, a thermometer, and a stirring device. The example shown in Figure A.1 is stirred by a plastic encased iron bar that, in turn, is moved by a water-impelled magnetic stirrer. However, stirring by hand yields the same results.

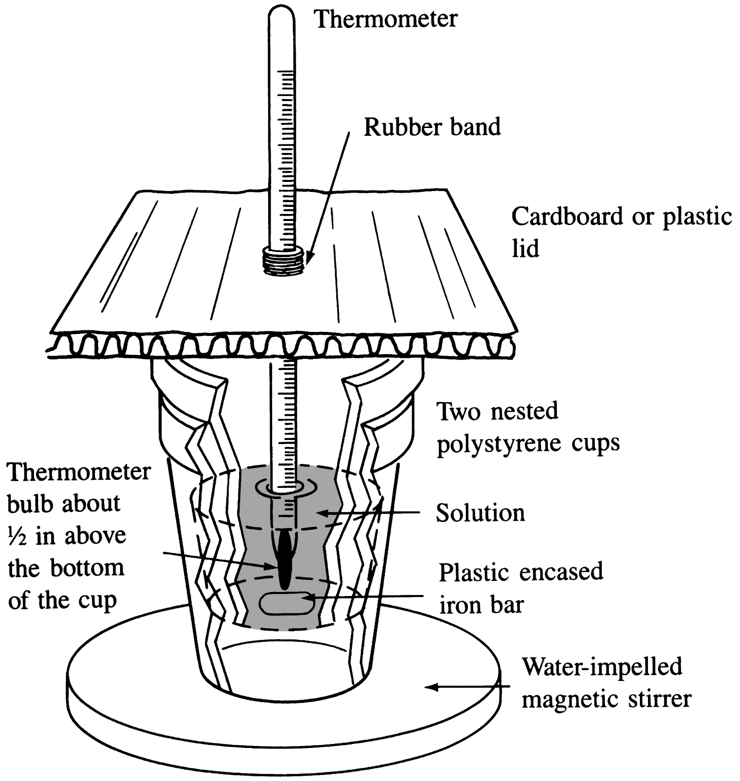

FIGURE A.1
The coffee-cup calorimeter. Mechanical stirring also can be used.

Like any other calorimeter, the coffee-cup calorimeter provides the means to measure the heat flow between a *system* and its *surroundings.* The meaning of these words must be understood in terms of our calorimeter.

Defining the surroundings and the system

We must begin by defining how much of the surrounding we will be required to consider. Can we limit the surroundings to a small region, or must we consider the entire laboratory?

The problem becomes rather simple if we assume that our calorimeter is perfectly insulated. Heat, we assume, will not flow through the walls of the calorimeter. This assumption allows us to restrict the extent of the surroundings. Because heat cannot flow out of or into the calorimeter, we can define the surroundings as the complete calorimeter and any water *whose temperature is* *initially identical to that of the calorimeter.* Later, we will find a way to correct for imperfect insulation without altering our definition of the surroundings.

The system includes any other substance or substances that are contained in the calorimeter. This definition of a system includes substances that are dissolved in the water, such as the reactants and products of a chemical reaction. It also includes other portions of water whose temperature is not initially identical to the temperature of the calorimeter.

An equation for heat flow

The equation that describes heat flowing between a system and its surroundings is

$$q(\text{system}) = -q(\text{surroundings})$$

This equation states that heat lost (or gained) by a system, q(system), is equal to heat gained (or lost) by the surroundings, $-q$(surroundings). Clearly, q(system) and q(surroundings) must have opposite signs, because as heat is lost by one, it is gained by the other.

Because of our definition of the surroundings, the equation for heat flow becomes

$$q(\text{system}) = -q(\text{water}) - q(\text{calorimeter})$$

The following equations show how the heat gained or lost by the water and the calorimeter, q(water) and q(calorimeter), can be calculated:

$$q(\text{water}) = \text{sp. ht.} \times \text{mass of } H_2O \times (t_f - t_i)$$

$$q(\text{calorimeter}) = C \times (t_f - t_i)$$

where sp. ht. is the specific heat, C is the heat capacity of the calorimeter, t_f is the final temperature, and t_i is the initial temperature. We will take the specific heat to be that of pure water, 4.184 J/(g • °C). Unless we are dealing with pure water, however, this is only an approximation. When substances are dissolved in the water, its specific heat is altered somewhat. We will also take the heat capacity of the calorimeter to be 1.0×10^1 J/°C.

An example

Suppose the temperature of 50 mL of 1.0 *M* NaOH in a coffee-cup calorimeter is 25.3°C. When 50 mL of 1.0 *M* HCOOH (formic acid), whose temperature is also 25.3°C, is added to the calorimeter, the temperature increases to 31.8°C. The chemical reaction is

$$NaOH + HCOOH \rightarrow NaHCOO + H_2O$$

The density of the final solution can be taken to be 1.0 g/mL. We will identify the surroundings and the system and then calculate q(system).

The surroundings are the complete calorimeter and all the water from both of the original solutions. Note that this water and the calorimeter share the same temperature. Thus the demands of our definition of the surroundings are met. The mass of this water is

$$(50 + 50)\ \text{mL} \times 1.0\ \text{g/mL} = 1.0 \times 10^2\ \text{g}$$

The system becomes the reactants and products of the chemical reaction, including the quantity of water that is formed in the reaction.

We will now calculate q(water) and q(calorimeter) from our equation for heat flow. We will use 4.184 J/(g • °C) as the specific heat of water and 1.0×10^1 J/°C as the heat capacity of the coffee-cup calorimeter.

$$\begin{aligned} q(\text{water}) &= 4.184\ \text{J/(g} \bullet {}^\circ\text{C)} \times 1.0 \times 10^2\ \text{g} \times (31.8 - 25.3)^\circ\text{C} \\ &= 2.7 \times 10^3\ \text{J} \end{aligned}$$

$$\begin{aligned} q(\text{calorimeter}) &= 1.0 \times 10^1\ \text{J/}^\circ\text{C} \times (31.8 - 25.3)^\circ\text{C} \\ &= 65\ \text{J} \end{aligned}$$

Then

$$\begin{aligned} q(\text{system}) &= -q(\text{water}) - q(\text{calorimeter}) \\ &= -2.7 \times 10^3\ \text{J} - 65\ \text{J} \\ &= -2.8 \times 10^3\ \text{J or } -2.8\ \text{kJ} \end{aligned}$$

Enthalpy changes

Enthalpy changes can be calculated by dividing q(system) by the number of moles of the limiting reactant. In our example, we have for each reactant

$$50\ \text{mL} \times 1\ \text{L}/10^3\ \text{mL} \times 1.0\ \text{mol/L} = 5.0 \times 10^{-2}\ \text{mol}$$

The enthalpy change becomes

$$\Delta H = -2.8\ \text{kJ}/5.0 \times 10^{-2}\ \text{mol} = -56\ \text{kJ/mol}$$

Correcting for imperfect insulation

The equation for heat flow was obtained using the assumption that our calorimeter is perfectly insulated. We must now recognize that this assumption is not warranted, because heat will flow through the walls. After all, hot coffee in a polystyrene coffee cup cools even if the top is covered.

Because heat leaks through the walls, we will not be able to observe the highest (or lowest) temperature that could have been achieved in a perfectly insulated calorimeter. However, we need to know that temperature, because it is t_f in our equation for heat flow.

We will estimate that temperature by plotting temperature as a function of time. We will then extrapolate to the time at which the solutions were mixed. This temperature is t_f. A typical result is shown in Figure A.2, which indicates how a final temperature of 31.8°C was estimated in the preceding example.

Note, however, that the rate and method of stirring affect the appearance of this graph.

FIGURE A.2

A graph showing the temperature as a function of time after 50 mL of 1.0 *M* NaOH and 50 mL of 1.0 *M* HCOOH are mixed.